



LYOLUMINESCENCE STUDY OF GAMMA-RAY IRRADIATED DY³⁺ ACTIVATED CaB₄O₇ PHOSPHORS FOR DOSIMETRY APPLICATIONS

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Abstract

CaB₄O₇ synthesis by solid state diffusion and its use in dosimeter applications are discussed in this paper. XRD characterization of the sample confirmed the formation of material and phases present in the sample. Photoluminescence (PL) of the sample was recorded to find the role of rare earth ions. Lyoluminescence (LL) study of the gamma-ray-irradiated sample was taken. A single distinct peak was observed in the LL glow curve of the phosphor sample. It is observed that LL increased almost linearly with gamma-ray exposures. LL intensity also increases linearly with the mass of the borate sample. Low fading is observed for the sample. These properties make this phosphor as a good candidate for LL dosimeter.

Keywords: Dosimeter, Luminescence, Lyoluminescence.

1. Introduction

Cold emission of light is called luminescence. The lyoluminescence produced when certain irradiated phosphor dissolved in suitable solvent [1]. The intensity of light produced is based on absorbed dose in the sample. The lyoluminescence phenomenon, owes its origin to the transfer of energy from the radiation-induced free radicals to the solvent molecules, a part of which is transposed to visible light. The LL phenomenon has been developed to find its applications as a system, especially for tissue equivalent dosimetry, detection of irradiated food materials, radiation damage studies in solids and in the search of irradiated food materials[2-5]. Up to now, much efforts has been taken to seek new and high efficient LL

material with the increasing need for dosimetry materials used in environment, personal, and clinical ionizing radiation protection. The luminescence studies of borate compounds are attractive because of their near tissue equivalent absorption coefficient. Investigations on a series of borate compounds have been reported, e.g., BaB₄O₇:Dy [6], Li₂B₄O₇:Cu,In [7], SrB₄O₇:Dy [8], MgB₄O₇:Dy,Na [9], Ba₂Ca(BO₃)₂:Tb [10] and Sr₂Mg(BO₃)₂ [11]. A new series of calcium containing rare-earth borates have been synthesized [12]. They have good thermal and chemical stability and are good host for luminescent material under UV excitation. Due to this we focussed on the Lyoluminescence study of gamma-ray irradiate Dy³⁺ activated CaB₄O₇ phosphors for dosimetry application.

2. Experimental Technique

Dy doped CaB₄O₇ phosphors were synthesised by solid-state diffusion method. In this technique proper quantity of calcium carbonate, boric acid and dysprosium oxide were grounded thoroughly in a pastel and mortar. The mixture was then heated at 725 °C for 12 hours and then cooled slowly. Obtained sample was grounded again then fired at 750 °C for another 12 hours then cooled slowly up to room temperature. The required size of the samples was obtained by crushing and sieving them. The test sieves are used to sieve out the crushed powder in to different size, samller particles are sieved out first whereas the larger particles are sieved out at the last. XRD pattern of the sample was recorded by X-ray defractometer (PW-1710). Photoluminescence (PL) of the rare earth doped samples were recorded using

spectrofluorophotometer (Shimadzu RF-5301 PC). The gamma-ray-irradiation was carried out using ^{60}Co source. A routine setup consisted of a photomultiplier tube and nano-ammeter was used to record LL.

3. RESULTS AND DISCUSSIONS

XRD Characterization:

XRD analysis has been carried out to recognize host material and phases present in the prepared phosphor. Figure 1 shows XRD pattern of CaB_4O_7 phosphor. XRD pattern obtained is almost similar to the JCPDS card No. 83-2025 and it may be concluded that small amount of impurity doped in the host material does not affect the XRD pattern.

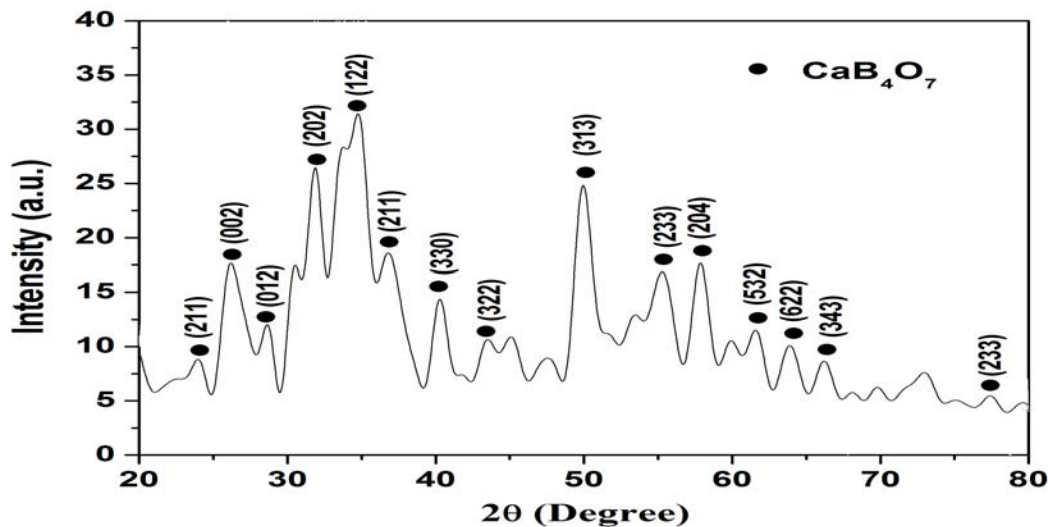


Figure 1 XRD pattern of the CaB_4O_7 : Dy poly-crystals.

PL characterization

The emission spectra of CaB_4O_7 :Dy phosphors is shown in figure 2. Two peaks around 470 nm and 580 nm are observed when phosphor is excited by the electromagnetic radiation of wavelength 354 nm. The emission of Dy^{3+} originates from the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_J$ ($J=7/2, 9/2, 11/2, 13/2$ and $15/2$) transitions in the visible and near infrared regions. Within these transitions, the yellow band at ~ 580 nm corresponding to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition and the blue band at 470 nm corresponding to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition are predominant. It is well

known that the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition is hypersensitive ($\Delta L=2, \Delta J=2$) and therefore, its intensity strongly depends on the host, where as intensity of the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition is less sensitive to the host. The ratio of yellow to blue intensity depends on the environment of Dy^{3+} ions. At a suitable ratio of yellow to blue emission, Dy^{3+} will emit nearly white, so that luminescent materials doped with Dy^{3+} may be used as potential two-primary-color phosphors (Su et al, 1993)[13].

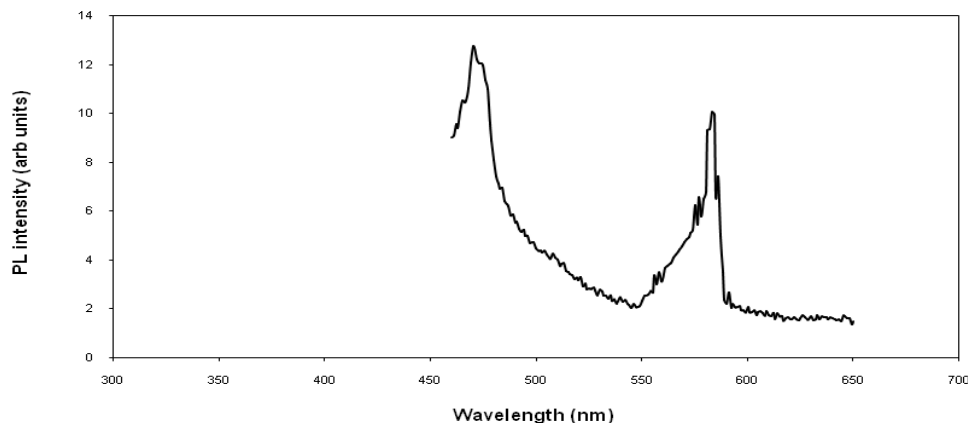


Figure 2: PL emission spectrum of CaB_4O_7 : Dy (2.0 mol%) phosphors under 354 nm excitation.

LL characterization

When the gamma-ray-irradiated $\text{CaB}_4\text{O}_7:\text{Dy}$ phosphors were dissolved in dilute hydrochloric acid having concentration 0.36 gm/l, LL intensity initially increased with time attained an optimum value and then decreased and finally disappeared. Figure 3 shows the dependence of LL intensity on the particle size of the sample. It is observed that The LL

intensity initially increases with increasing particle size of the sample and above a certain particle size the LL intensity decreases with increase in particle size. This may be due to greater stability of defect centres in crystallites of large dimensions whereas in the case of smaller dimensions there is a rapid decay of defect centre resulting in poor radiolysis products.

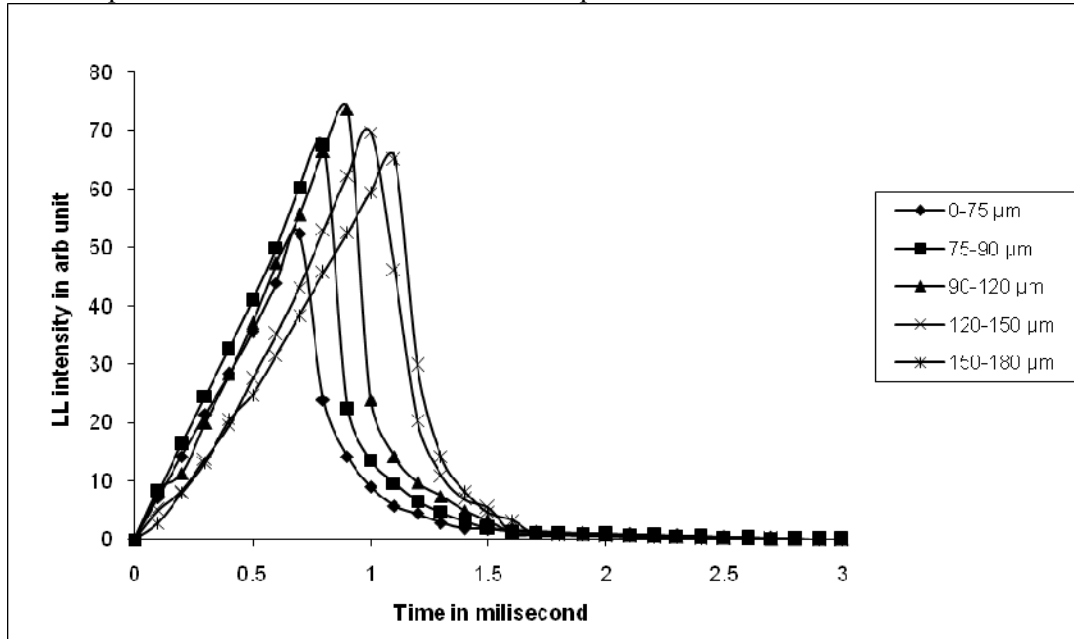


Figure 3: Time Dependence of LL intensity of γ -ray irradiated $\text{CaB}_4\text{O}_7:\text{Dy}$ (2.0 mol%) phosphors for various particle size. γ -ray dose 1.1 kGy when dissolved in dilute (.36 gm/l) hydrochloric acid.

Fig.4: shows the variation of LL intensity with gamma ray exposure of $\text{CaB}_4\text{O}_7:\text{Dy}$ (2.0 mol%) phosphors. It is observed that the LL intensity increases with gamma ray dose given to the samples and attains saturation for higher values of gamma doses.

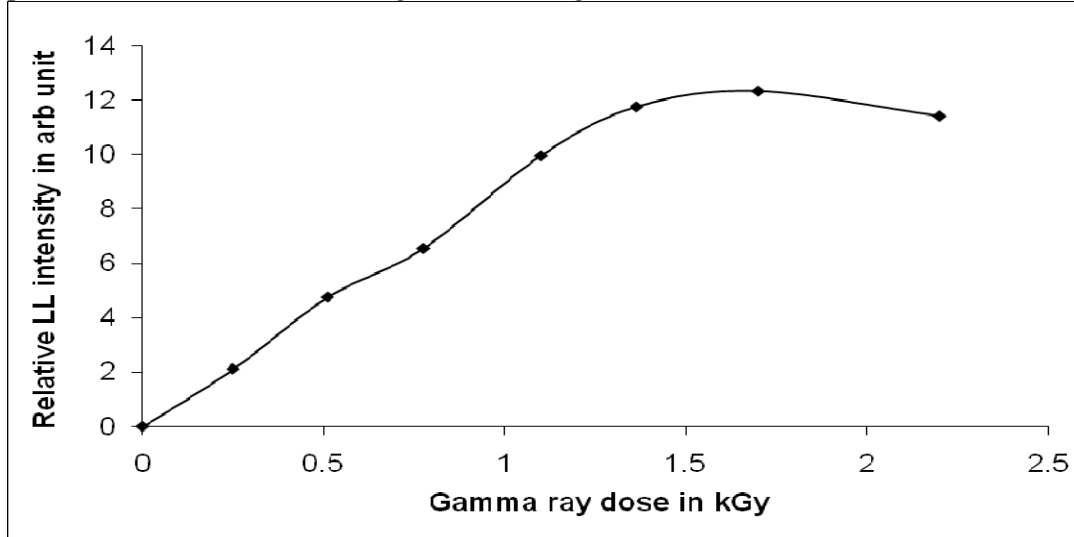


Figure 4: Variation of peak LL intensity with different γ -ray dose.

Fig. 5 shows the effect of storage on LL (at room temperature in dark) of γ -irradiated CaB_4O_7 : Dy (2.0 mol%) phosphors. It is clear that fading in LL intensity of the entire sample is very low.

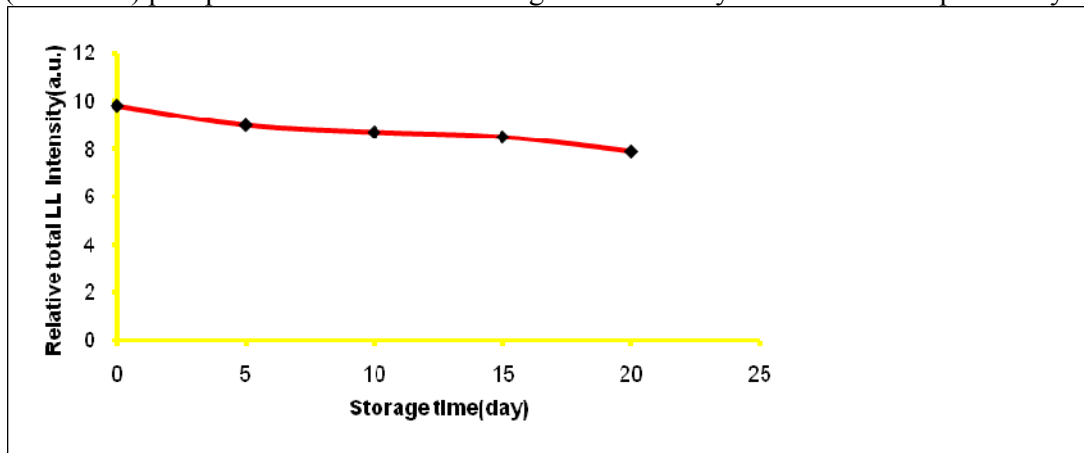
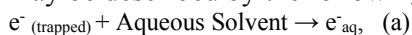


Fig. 5 Effect of storage on the LL glow peak in CaB_4O_7 : Dy (2.0 mol%) phosphors exposed to γ -ray dose 1.1 kGy.

Borates under γ -rays irradiation are known to produce various defect centers such as B^{2+} , BO_3^{2-} , O^- , $(\text{B}_3\text{O}_6)^{3-}$, O_3^- , O_2^- etc [14-15]. On dissolving such borates in suitable solvent the LL is observed due to release of trapped energy during dissolution [16-23]. Schematically, the mechanism of LL in CaB_4O_7 : Dy (2.0 mol%) may be described by the following equations:



where, X = Radicals generated due to γ -rays irradiation.

The number of hydrated electrons will increase due to the dissolution of the crystallites and it will decrease due to the recombination of hydrated electrons with the holes present on the surface of the crystallites.

In the observation of the dependence of LL intensity on the γ -irradiation dose given to the CaB_4O_7 : Dy (2.0 mol%) crystal, It is seen that initially the LL intensity increases with the radiation dose and then it attains a saturation value for higher radiation doses given to the crystallites. This can be understood as follows:

When a CaB_4O_7 : Dy (2.0 mol%) crystal is exposed to high energy radiation like γ -rays or X-rays, excitation of electrons of borate atoms from valence band to conduction band takes place. Some of the excited electrons return immediately from the conduction band to the valence band, however, some of the electrons in the conduction band get trapped in

the negative ion vacancies during their movement and consequently the formation of defect centres takes place. Initially the number of defect centres increases with the radiation dose given to the crystals and thereby, the LL intensity increases with the radiation dose. However, for long duration of the irradiation of the crystals the recombination between electrons and holes takes place and consequently the density of defect centres in the crystals attains a saturation value.

As a matter of the fact, the LL intensity also attains a saturation value for high radiation dose given to the crystallites.

4. Conclusion

CaB_4O_7 : Dy (2.0 mol%) phosphor was synthesized via a solid state reaction process. Well crystallized powders were obtained. A single peak is observed in its LL glow curve which indicates the formation of only one type of luminescent centre in the host material. It is observed that an enhancement in LL intensity depends on the defect centre concentration in the powder sample. The increment of LL may be due to greater stability of luminescence centers in crystallites of large dimension. And the decrement of LL with increasing particle size is because rate of dissolution decreases with increasing grain size. The LL intensity increases sub linearly with gamma ray dose. It also shows very low fading in LL intensity on storage. Experimental results suggest that this phosphor may be useful for LL dosimetry with low cost.

5. References

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